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Bioscouring of linen fabric in comparison with conventional chemical treatment

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ABSTRACT

Enzymatic scouring of linen fabric using a mixture of pectinase and lipase is described. For comparison, a sample of linen fabric was scoured conventionally in boiling alkaline solution. The enzymatically scoured linen fabric showed lower loss in weight than the conventionally scoured one but on the other hand, its drop penetration time was found to be too high. After common bleaching, the wettability and the degree of whiteness of both the enzymatically and the conventionally scoured linen fabrics were found to be similar. In contrast to the harsh conditions applied in the alkaline scouring, during the gentle enzymatic procedure, significant lower fiber damage occurs resulting in better mechanical properties, such as a higher degree of polymerization and an increased tensile strength. After scaling-up the suggested enzymatic treatment of linen fabric, promising ecological and economical benefits could be attained.

1. Introduction

Conventional pre-treatment steps in cotton processing could be successfully substituted by enzyme-catalyzed processes many years ago. Compared with chemical treatments, biotreatment is a more eco-friendly alternative to remove non-cellulosic impurities from cotton fibers by using specific enzymes to make the surface more hydrophilic. Waxy materials and pectins are responsible for the hydrophobic nature of raw cotton, which in turn greatly affect the further chemical processing, such as dyeing and finishing. Like cotton, also other natural fibers such as hemp or flax contain undesired components in their primary wall, which have to be removed before the following finishing, especially pectins, waxy materials and hemicelluloses. A mature flax cell wall consists of 70–75% cellulose, 15% hemicelluloses and 10–15% pectic materials. Both the hemicellulosic and pectic materials play important roles in fiber bundle integration, fiber bundle strength and individual fiber strength. The bulk of literature to date has looked at the pectic material since this is thought to be responsible for binding the cell wall layers together and is present in high concentrations in the middle lamella. Pectin builds a network with its structure, and the other impurities such as proteins and waxes are dispersed through the backbone and side chains of pectin (Sawada, Tokino, Ueda, & Wang, 2003).

It is now generally accepted that the pectin and wax contents, and the distribution of the latter, are responsible for the non-wetting behavior of cellulosic fibers by water. Bioscouring refers to the enzymatic-catalyzed removal of pectins and waxes from the surface of cellulosic fibers, which results in bleaching and dyeing improvement. This process preserves the fiber's structure and strength, and avoids the high energy consumption and severe pollution problems that are associated with conventional alkaline treatments.

Previous work in the area of cotton bioscouring has been focused on investigating the utility of various enzymes. Although several types of enzyme including pectinases, (Calafell & Garriga, 2004; Choe, Nam, Kook, Chung, & Cavaco-Paulo, 2004; Csiszar, Losonczi, et al., 2001; Ibrahim, El-Hossamy, Morsy, & Eid, 2004; Karapinar & Sariisik, 2004; Klug-Santner et al., 2006; Sawada & Ueda, 2001; Sheth & Musale, 2005; Wang, Fan, Hua, & Chen, 2007) cellulases, (Aly, Moustafa, & Hebeish, 2004; Csiszar, Losonczi, et al., 2001; Csiszar, Urbanszki, & Szakacs, 2001) proteases, (Karapinar & Sariisik, 2004) xylanases, (Csiszar, Losonczi, et al., 2001; Csiszar, Urbanszki, et al., 2001) have been studied, pectinases were found to be the most effective and suitable for cotton bioscouring. The mechanism of pectinase scouring reportedly assumes that the degradation and elimination of pectins make the loosened waxes more easily removable with the help of surfactants and mechanical agitation; this allows the cotton to achieve superior hydrophilicity without fiber deterioration.

Therefore investigations were carried out in the present work with the aim of transferring the excellent experience from cotton pre-treatment with a mixture of enzymes to the bast fibers pre-treatment.

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2. Experimental

2.1. Materials

For the enzymatic treatment of linen fabric (plain weave, 169 g/m^2), pectinase from *Aspergillus niger* (Fluka), lipase from *Candida cylindracea* (Aldrich) and citric acid/sodium hydroxide buffer solution (pH 5) were used. For conventional alkaline scouring and bleaching of linen fabric, sodium hydroxide, sodium carbonate, non-ionic surfactant (Marlipal O13/80), hydrogen peroxide, sodium silicate and magnesium sulphate were used.

2.2. Bioscouring

Linen fabric samples (1 g each) were treated separately in citric acid/sodium hydroxide buffer solutions (pH 5) containing different amounts of 1:1 pectinase:lipase enzymes using a material to liquor ratio of 1:30. Control sample was treated with the same buffer solution using the same material to liquor ratio but without adding any enzyme dose. The incubation was carried out in a temperature-controlled shaker at 50 °C for 3 h. In order to stop the enzyme action, the fabrics were dipped in boiling water for 3 s. The samples were then washed thoroughly with cold water and finally air dried.

The evaluation of the bioscouring result was performed by carrying out the Ruthenium Red dyeing test and monitoring both the weight loss percent and the water absorbency of the treated fabric samples as a result of the enzymatic process.

2.3. Ruthenium Red dyeing

Residual pectin on the fabric is analyzed by staining with Ruthenium Red dye (Novozymes, 2003). Briefly, the bioscoured linen sample was sewed with a grey linen fabric sample (100% pectin control). The sewed fabrics were then dyed with Ruthenium Red dye solution for 15 min at room temperature and rinsed thoroughly with water at 60 °C and finally air dried overnight.

2.4. Conventional alkaline scouring

The linen fabric was boiled in an aqueous solution containing 5 g/l NaOH, 3 g/l Na_2CO_3 and 1.5 ml/l Marlipal O13/80, under reflux for 60 min using a material to liquor ratio of 1:20. After the alkaline treatment, the fabric was washed three times with boiling water, twice with cold water and finally air dried.

2.5. Common bleaching

Both the conventionally and the enzymatically scoured linen samples were boiled, separately, in an aqueous solution containing 3 g/l H_2O_2, 1.5 g/l NaOH, 6 g/l sodium silicate, 0.2 g/l $MgSO_4$ and 0.2 ml/l Marlipal O13/80, under reflux for 60 min using a material to liquor ratio of 1:20. After the bleaching treatment, the fabric was washed three times with boiling water, twice with cold water and finally air dried.

2.6. Testing and analyses

2.6.1. Weight loss

Fabric weight loss was calculated on the basis of dry weight using the following equation:

$$\%\text{weight loss} = (W1 - W2) \times 100/W1,$$

where $W1$ and $W2$ are the dry weights of the fabric before and after treatment, respectively.

2.6.2. Fabric wettability

The wettability of the linen samples was measured using the drop penetration test (Arbeitsgruppe, 1987).

2.6.3. Degree of polymerization

The average degree of polymerization (DP) was determined according to DIN 54270-T3.

2.6.4. Tensile strength

The tensile strength and elongation at maximum force were measured according to DIN 53857.

2.6.5. Degree of whiteness and colour strength

The degree of whiteness (Berger) of the linen fabrics after bleaching and the colour strength of fabrics stained with Ruthenium Red dye were measured using a Datacolor unit.

2.6.6. UV measurement

The UV–vis-spectra of grey and bleached (conventionally scoured and bioscoured) linen fabrics were measured using Cary UV–vis-NIR Spectrophotometer.

2.6.7. Scanning electron microscopy

The morphological structure of grey and differently pre-treated linen fabrics was evaluated by SEM with a Hitachi S-3200N scanning electron microscope.

2.6.8. Infrared spectroscopy

The infrared spectra of grey and bleached (conventionally scoured and bioscoured) linen fabrics were measured using a Perkin-Elmer 2000 FT-IR spectrometer.

3. Results and discussion

3.1. Enzymatic treatment of linen fabric

Table 1 shows weight loss percent and wettability of linen fabrics treated with different amounts of 1:1 (pectinase:lipase) mixture. The results show improved wettability compared with the grey fabric, and increased weight loss percent by increasing the enzyme mixture concentration.

Another important proof for the successful enzymatic removal of the disturbing constituents from the bioscoured fabric is the decreased colour strength of the fifth linen sample (Table 1) compared to that of the grey material after dyeing with Ruthenium Red, which only colours pectin but not the cellulosic material. The colour strength (K/S) falls from 20.81 in case of grey fabric to 12.39 in case of enzymatically scoured fabric.

3.2. Enzymatic scouring in comparison with alkaline scouring

Properties of linen fabric treated gently with a mixture of pectinase and lipase, at a pH-value near the neutral and low-temperature (fifth sample in Table 1) were measured and compared with

Table 1
Wettability and % weight loss of bioscoured linen fabrics

Serial	Enzyme dose pectinase g/l + lipase g/l	Weight loss percent	Wettability (min:s)
1	1.5 + 1.5	1.687	12:49
2	2.5 + 2.5	1.823	10:06
3	5 + 5	2.234	7:20
4	6. + 6	2.305	5:30
5	8 + 8	2.487	3:05
Control	–	0.319	30:00
Grey	–	0	33:52

the corresponding properties of grey linen fabric and conventionally scoured linen fabric treated in highly alkaline solution at the boil. The results are summarized in Table 2.

The enzymatically scoured fabric exhibits much better wettability than the original grey material, but it is still insufficient compared with that of the alkali scoured fabric. Indeed, the conventional procedure removes most of the disturbing linen constituents, but it also destroys some of the cellulosic chains of the fiber resulting in poor degree of polymerization (2608), bad mechanical properties and even high weight loss of 10%. The gentle enzymatic treatment causes no cellulose hydrolysis. The relative weight loss amounts only to 2.5% and the degree of polymerization decreases merely from 3119 to 2961. That is why the mechanical properties (tensile strength and elongation at maximum force) of the enzymatically scoured linen sample are significantly better than those of the conventionally scoured one. These results are also supported by the micrographs of grey, alkali scoured and bioscoured linen fabrics (Figs. 1–3). The SEM micrographs can clearly demonstrate the fiber damage accompanied with the harsh alkaline scouring in comparison with the gentle action of the enzymatic procedure. This is another evident that in case of alkaline scouring, random hydrolysis occurs even in the basic cellulosic fibers and not only the undesired materials while in case of enzymatic scouring, the action of enzyme is specific in removing only the undesired non-cellulosic materials.

Table 2
Properties of grey, enzymatically scoured and conventionally scoured linen fabrics

Property	Grey linen fabric	Alkali scoured linen fabric	Bioscoured linen fabric
Drop penetration time (min:s)	33:52	<00:03	3:05
Weight loss (%)	–	10.0	2.5
Degree of polymerization	3119	2608	2961
Tensile strength (daN)	78.4	60.1	68.3
Elongation at F_{max} (%)	7.4	6.0	6.8

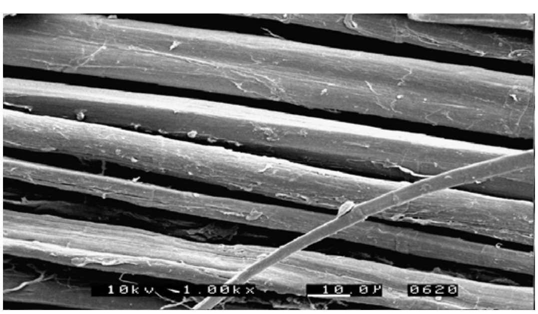

Fig. 1. SEM micrograph of grey linen fiber.

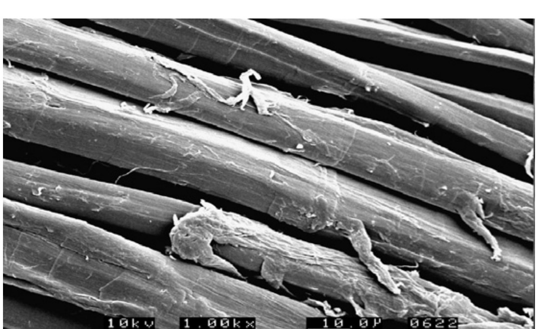

Fig. 2. SEM micrograph of alkali scoured linen fiber.

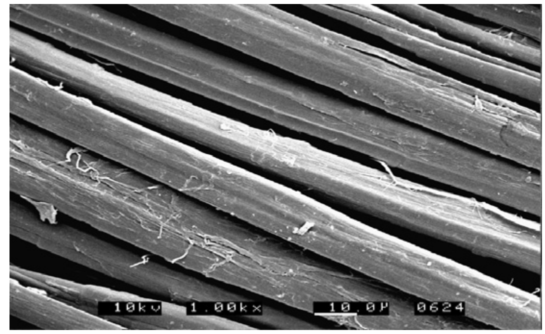

Fig. 3. SEM micrograph of bioscoured linen fiber.

3.3. Fabric properties after common bleaching

As shown in Table 2 the drop penetration time of the enzymatically treated material is still too high indicating that not all pectins and lipids are removed yet. As a rule, the conventional pre-treatment of linen is not completed with the alkaline scouring due to the fact that the coloured compounds of linen are not removed hereby. Therefore a subsequent bleaching step is necessary. Accordingly the differently scoured linen fabrics (enzymatically and conventionally) are bleached, separately, in a common way using hydrogen peroxide at high temperature and high pH-value.

Infrared spectra of representative samples of grey and bleached (enzymatically scoured and conventionally scoured) linen fabrics were measured (Figs. 4–6) to show the effect of bleaching after both treatments on the extent of remaining non-cellulosic materials removal from linen fabrics. The effect was simply estimated through noticing the characteristic peak of the residual pectin.

The figures show clear peaks for pectin at 1730 cm^{-1}. The figures show also noticeable difference between the pectin peak corresponding to grey linen fabric and the two peaks corresponding to bleached fabrics (conventionally scoured and bioscoured). On the other hand, it is clear from the two peaks corresponding to the two bleached fabrics that the residual pectine after bleaching is almost the same in both enzymatically and conventionally scoured fabrics.

Fig. 7 shows the UV–vis-spectra of the grey material in comparison with the bleached linen fabrics (conventionally scoured and bioscoured). As expected, in general the remission of the bleached linen fabrics is much higher than that of the original grey material. Qualitatively, there is no difference in the absorbance behavior between the differently scoured linen fabrics after common bleaching, showing that the visual properties are good in both cases.

Table 3 summarizes the most important properties of the differently scoured linen samples after common bleaching. First of all, after bleaching, both the enzymatically and the conventionally scoured fabrics show no difference in the degree of whiteness according to Berger (nearly 66). Also, the wettability of both materials after bleaching is excellent (<3 s). This proves that the remaining hydrophobic residues such as pectins and lipids are removed completely together with the colouring materials after bleaching. This complete removal is due to the improved accessibility of the fabric for the bleaching chemicals in both the enzymatic and conventional scouring. Moreover, the weight loss in total (the sum of weight losses due to scouring and bleaching), after bleaching of the conventionally scoured fabric amounts to more than 12% indicating random hydrolysis of the treated material, which might damage the cellulosic fibers. Accordingly, the degree of polymerization falls to 2066 and this corresponds to a loss in DP of about one third compared with the original grey fabric. The enzymatically pre-treated fabric shows much better mechanical properties

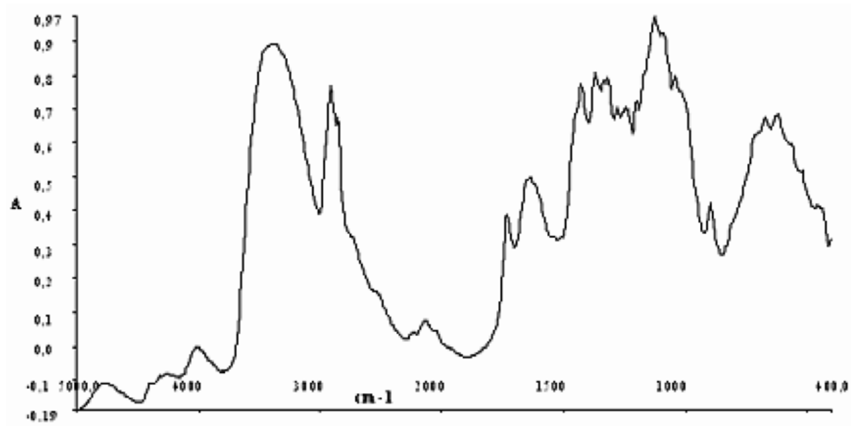

Fig. 4. Infrared spectrum of grey linen fabric.

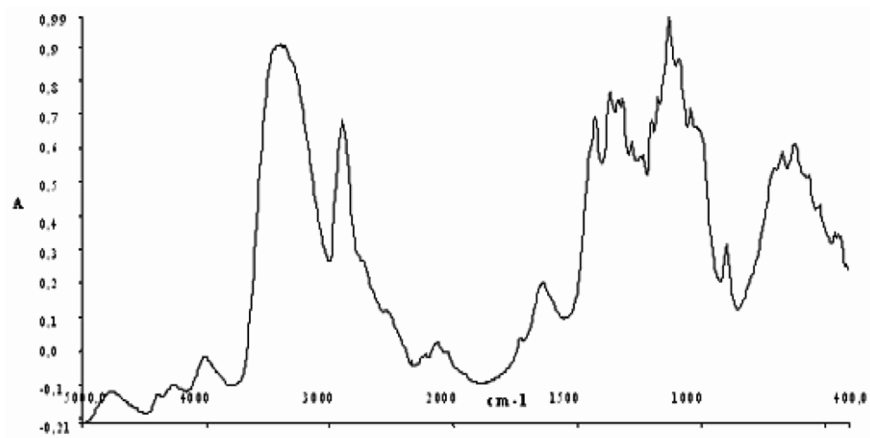

Fig. 5. Infrared spectrum of bleached linen fabric (alkali scoured).

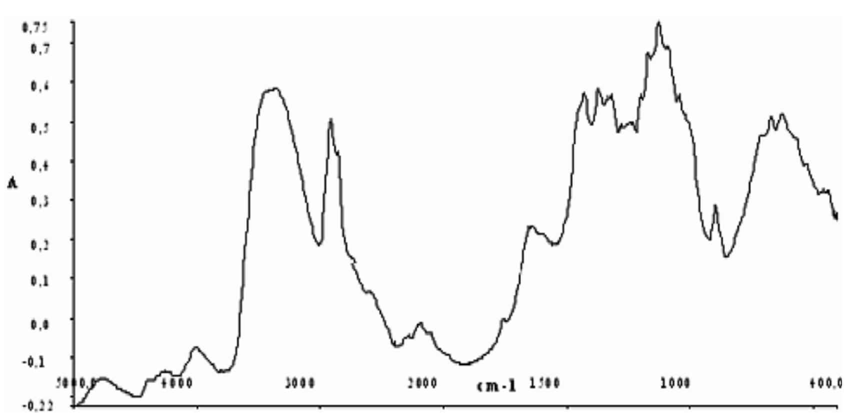

Fig. 6. Infrared spectrum of bleached linen fabric (bioscoured).

even after bleaching and the weight loss amounts only to 6.8% after scouring and bleaching.

4. Conclusion

A successful strategy for the use of an enzyme mixture (pectinase/lipase) in the pre-treatment of linen fabric was developed relying on the previous experience in enzymatic treatment of cotton. This knowledge gained from the enzymatic treatment of cotton fabrics could be adapted to treatment of linen fabric. Pectinase/lipase mixture was found to be capable of hydrolyzing the hydrophobic compounds in the primary wall of the linen fibers, which could be completely removed in a following conventional bleaching step using hydrogen peroxide. It can be shown that the enzymatically scoured linen fabric has similar or even better properties, after common bleaching, than the conventionally scoured material. After common bleaching, neither the wettability nor the degree of whiteness for the enzymatically scoured material are worse than those for the conventionally scoured linen fabric. Moreover, the material is treated more gently and shows better

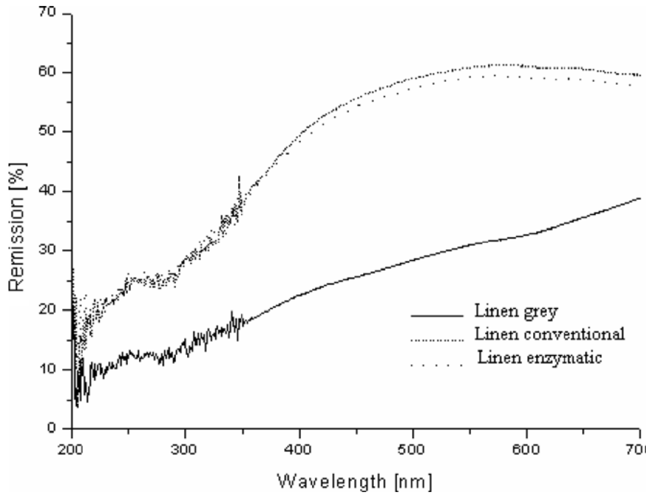

Fig. 7. UV–vis-spectra of grey linen fabric and bleached (conventionally scoured and bioscoured) linen fabrics.

Table 3
Properties of bleached (conventionally scoured and bioscoured) linen fabrics

Property	Grey linen fabric	Bleached linen fabric (alkali scoured)	Bleached linen fabric (bioscoured)
Drop penetration time (min:s)	32:52	<00:03	<00:03
Weight loss (%)	–	10.0 + 2.3 = 12.3	2.5 + 4.3 = 6.8
Degree of polymerization	3119	2066	2586
Tensile strength (daN)	78.4	48.1	52.8
Elongation at F_{max} (%)	7.4	5.9	6.0
Degree of whiteness (Berger)	22.4	66.0	65.9

mechanical properties. The new low-temperature enzymatic procedure is characterized by a significant lower demand of energy and chemicals. So it has advantages in terms of ecology. Moreover, optimizing this process and transferring it to an industrial scale should be also advantageous in terms of economy.

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